

## Vibrational spectra, conformations, quantum chemical calculations and spectral assignments of 1-chloro-1-silacyclohexane

Valdemaras Aleksa<sup>a,b</sup>, Gamil A. Guirgis<sup>c</sup>, Anne Horn<sup>a</sup>, Peter Klæboe<sup>a,\*</sup>, Richard J. Liberatore<sup>c</sup>, Claus J. Nielsen<sup>a</sup>

<sup>a</sup> CTCC, Department of Chemistry, University of Oslo, P.O. Box 1033, NO-0315 Oslo, Norway

<sup>b</sup> Department of General Physics and Spectroscopy, Vilnius University, Vilnius 2734, Lithuania

<sup>c</sup> Department of Chemistry & Biochemistry, College of Charleston, Charleston, SC 29403, USA

### ARTICLE INFO

#### Article history:

Received 21 November 2011

Received in revised form 27 February 2012

Accepted 29 February 2012

Available online 10 March 2012

#### Keywords:

Infrared and Raman spectra

Conformations

DFT calculations

1-Chloro-1-silacyclohexane

### ABSTRACT

The infrared spectra of 1-chloro-1-silacyclohexane have been studied as a vapour and liquid at ambient temperature and as amorphous and annealed crystalline solids at 78 K. Various infrared bands present in the vapour and liquid states vanished in the crystalline state upon cooling. Raman spectra of the liquid were recorded at 293 K and polarization data obtained. Additional Raman spectra were recorded at various temperatures between 293 and 163 K, and intensity changes with temperature of certain Raman bands were detected. A crystalline phase was observed around 140 K, leading to spectral shifts and a number of vanishing bands.

The compound exists in two conformers, *equatorial* (*e*) and *axial* (*a*) in the fluid phases, but only the *a*-conformer was present in the crystal. The experimental results suggest that the *a*-conformer has 2.8 kJ mol<sup>-1</sup> lower enthalpy than *e* in the liquid, leading to 69% of the *a* conformer at 293 K.

B3LYP calculations with various basis sets and the G3 model chemistry gave conformational energy difference  $\Delta E(e-a)$  in the range 0.4–1.4 kJ mol<sup>-1</sup>. Infrared and Raman intensities, polarization ratios and vibrational frequencies for the *e* and *a* conformers were calculated. The fundamental wavenumbers were also derived in the anharmonic approximation in B3LYP/cc-pVTZ calculations, a relative deviation of less than 2% between the observed and calculated wave numbers for the 48 modes of the *e*- and *a*-conformers was obtained.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

It has been established from numerous studies that the low energy form for the cyclohexane ring is the chair conformation whereas the additional craddle and twisted forms have much higher energies. They are therefore not observed under ordinary conditions, but have been identified by matrix isolation studies close to He temperature. In monosubstituted [1] and in 1,4-disubstituted cyclohexanes [2] the *equatorial* (*e* or *ee*) conformers have usually lower energies than the *axial* (*a* or *aa*) conformer, leading to a larger abundance of the *e* (*ee*) conformers in the vapour and in the liquid states. In the crystalline state obtained by cooling the liquids, these cyclohexanes generally exist only in the *e* (*ee*) conformers since the *a* (*aa*) conformers are not accommodated in the crystal lattice.

When a carbon atom in cyclohexane is substituted with silicon, the steric and electronic effects are changed. However, much

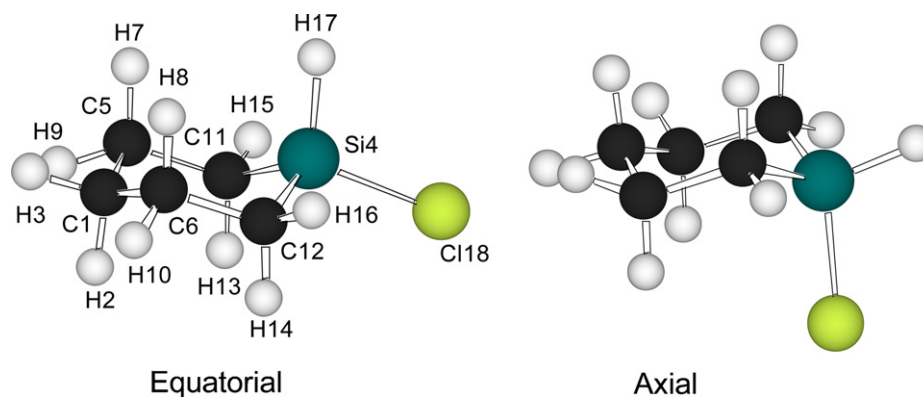
less experimental information is available since these compounds are more unstable than the corresponding cyclohexanes and their preparations are difficult. The parent molecule silacyclohexane and a few molecules with an atom substituted on the silicon have been investigated [3].

Quantum chemical calculations on silacyclohexane and on substituted silacyclohexanes revealed the chair form to be the dominant conformer relative to the boat and twist forms [4–6] similar to the cyclohexanes. From quantum chemical calculations it has been established [7,8] that unlike the cyclohexanes most of the monosubstituted silacyclohexanes have the *a* conformer as the preferred form (Fig. 1).

Among the monosubstituted silacyclohexanes, 1-fluoro-1-silacyclohexane has been investigated by microwave spectroscopy [9], gaseous electron diffraction, low temperature NMR spectroscopy, Raman spectroscopy and by quantum chemical calculations [10]. All these techniques have revealed that the *a* conformer has more than 1 kJ mol<sup>-1</sup> lower energy than the *e* form in this compound. An exception is presented by 1-methyl-1-silacyclohexane in which gaseous electron diffraction and NMR spectroscopy in solution gave an abundance of 68% in the vapour phase and 74% in

\* Corresponding author. Tel.: +47 22855678; fax: +47 22855441.

E-mail address: [peter.klaeboe@kjemi.uio.no](mailto:peter.klaeboe@kjemi.uio.no) (P. Klæboe).



**Fig. 1.** The equatorial (*e*) and axial (*a*) conformers of 1-chloro-1-silacyclohexane (CSC), including numbering of atoms for the definition of symmetry coordinates.

solution of the *e*-conformer [11], supported by quantum chemical calculations.

In this study we present an infrared and Raman spectroscopic investigation of 1-chloro-1-silacyclohexane (later to be abbreviated CSC), with special emphasis on the conformational equilibrium between the *e* and *a* conformers. In a very recent short communication the molecular structure of CSC was investigated by gaseous electron diffraction and by quantum chemical calculations [12]. The results obtained by vibrational spectroscopy and by DFT calculations for CSC are compared with the results for chlorocyclohexane, a molecule studied by many authors with different experimental techniques.

## 2. Experimental

### 2.1. Preparation

The sample of 1-chloro-1-silacyclohexane (CSC) was prepared by the formation of a double Grignard of 1,5-dibromopentane in dry ethyl ether. The Grignard was then coupled with freshly distilled trichlorosilane in dry ethyl ether overnight with refluxing. The magnesium salt was separated from the ethereal solution by filtration under dry nitrogen. The ether was distilled off at reduced pressure and the final purification was obtained by a trap to trap distillation.

The purity of the sample was checked by infrared spectra, having characteristic absorptions of Si–H and Si–Cl stretching bands (see below). In  $^{13}\text{C}$  NMR spectra in  $\text{CDCl}_3$  solution three signals for carbons with the correct positions in the spectrum were observed, 14.99 (C2 and C6), 23.32 (C3 and C5) and 29.26 ppm (C4).

### 2.2. Infrared measurements

The mid infrared spectra (MIR) were recorded on two Fourier transform spectrometers: a Bruker spectrometer Vertex 80 and a Perkin-Elmer model 2000 ( $4000\text{--}400\text{ cm}^{-1}$ ). Additional far infrared (FIR) spectra were obtained using the Vertex 80 spectrometer in the FIR set-up ( $600\text{--}100\text{ cm}^{-1}$ ). Both spectrometers had DTGS detectors, beamsplitters of Ge coating on a KBr substrate were employed in the MIR region and a multilayer coating on Mylar in the FIR region. The spectrometer was flushed with dry nitrogen gas to diminish the absorption of water vapour in the FIR region.

The vapour was studied in cells with CsI windows (10 cm path) in the MIR region and polyethylene windows (18 cm path) in the FIR range. MIR spectra of the liquid were recorded as a capillary between two KBr windows, and FIR spectra in a closed cell of polyethylene (throw away cell) of ca. 0.2 mm path.

The vapour was deposited on a CsI window, cooled with liquid nitrogen, but initially no crystallization was observed on the window. The sample was annealed to various temperatures between 120 and 150 K and recooled to 78 K before recording of the spectra. When heated above 160 K the sample melted.

### 2.3. Raman measurements

The Raman spectra were recorded with a multichannel spectrometer from Horiba (Jobin Yvon) model T 64000 employing both single and triple monochromator detection. The spectrometer was fitted with a CCD detector, cooled to ca. 130 K. The spectra were excited by a Millennia Pro diode-pumped (Nd:YVO<sub>4</sub> crystal) laser from Spectra-Physics (Model J 40), using 90 degrees scattering geometry, adjusted to give approximately 50 mW of the 532 nm line on the sample. The spectrometer was applied with different optical set ups: (1) a single monochromator using a notch filter, a triple monochromator with (2) additive or (3) subtractive collection. The different systems of light collection gave quite similar spectra, but the low wavenumber modes were recorded to  $60\text{ cm}^{-1}$  with the triple subtractive mode, compared to  $120\text{ cm}^{-1}$  with the single monochromator and the notch filter.

The high sensitivity of the CCD detector gave spectra with large signal/noise ratio, and the spectra were recorded at ca.  $2\text{ cm}^{-1}$  resolution. Depolarization measurements were recorded in the  $90^\circ$  illumination mode, employing a polarizer and a scrambler between the sample and the monochromator. The polarizer unit was calibrated with carbon tetrachloride, filled into a cylindrical tube identical to that employed for CSC. Except for very weak and/or overlapping bands, comprehensive depolarization data were obtained.

Raman spectra of the liquid, including depolarization measurements were primarily recorded at room temperature. Additional spectra were obtained for each 10 degrees between 293 and 163 K in a tube of 2 mm inner diameter. The sample tube was surrounded by a glass Dewar and cooled with gaseous nitrogen evaporated from a tank and controlled by an Eurotherm controller, using a calibrated Fe-constantan thermocouple [13] touching the tube and giving approximately  $\pm 0.2^\circ\text{C}$  accuracy.

From these spectra, the enthalpy difference  $\Delta_{conf}H^\circ$  between the conformers in the liquid were calculated. Various *e/a* band pairs were tested for determining the enthalpy difference, giving rather different values. If the capillary was cooled below 160 K the sample appeared turbid and below 150 K it slowly crystallized. The vapour of CSC was also condensed on a copper finger at 78 K. An amorphous phase was formed, and the bands were quite similar to those of the liquid. The sample was heated in steps to 130–150 K and it could

Download English Version:

<https://daneshyari.com/en/article/1250525>

Download Persian Version:

<https://daneshyari.com/article/1250525>

[Daneshyari.com](https://daneshyari.com)